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Some Experiments in Precision Colorimetry

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The precisions of measurements in the differential method and in the trace analysis method were studied. The differential method has a precision comparable to the gravimetric or volumetric method at high concentration. Similarly, the trace analysis method seems to be precies in the determination of low concentration, but its precision is not greater than that of the conventional method.

INTRODUCTION

In the spectrophotometric determination, three other methods have been proposed besides the conventional method. One of them is a differential or transmittance ratio method, in which a standard solution having known concentration, C_1, is used as the reference zero absorbance solution for the reagent blank. Another method, in which the reagent blank is used as zero-absorbance reference and a standard solution having known concentration, C_2, is used as the reference of zero-transmittance, is called a trace analysis method. In the third method, the general method, two standard solutions are used as the references of zero-absorbance and zero-transmittance.

The authors studied the precisions of the differential and trace analysis methods.

APPARATUS AND MATERIALS

Spectrophotometric measurements were made with a Beckman Quartz Spectrophotometer Model DU, using 1 cm silica cells.

Potassium permanganate solution : $KMnO_4$ solution of $10^{-4}M$ was prepared by diluting the stock solution, strandardized with oxalic acid.

Standard phosphoric acid solution, 1.00 mg P_2O_5/ml : 81.0 mg of $NH_4H_2PO_4$ was dissolved in water and diluted to 500 ml.

Perchloric acid, 5*M*-$HClO_4$.

Ammonium metavanadate solution, 0.02 *M*: 1.17 g of NH_4VO_3 was dissolved in warm water, after cooling 25 ml of 8 *M*-$HClO_4$ was added and diluted to 500 ml with water.

Ammonium molybdate solution, 0.2 *M*: 35.3 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was dissolved in water and diluted to 1,000 ml.

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EXPERIMENTAL

1. Differential Method

The differential method was proposed and developed by Hisky, Bastian, and their coworkers[1], and has been applied to the precision colorimeric determination of copper, nickel, manganese, iron, uranium *etc.*

In the conventional spectrophotometric method, if absolute error of the transmittance reading is independent of the transmittance value and Lambert-Beer's law is followed, the error in the determination of the concentration may be expressed as

$$\frac{\Delta C}{C} = -\frac{0.434}{Ts \cdot As} \Delta Ts \tag{1}$$

where $\Delta C/C$ is relative error in the concentration, Ts and As are transmittance and absorbance of measured solution, respectively, and ΔTs is absolute error of the reading in transmittance.

Therefore, the minimum error is produced if absorbance As is equal to 0.434 or transmittance Ts becomes 36.8 percent.

In the differential method, however, the error function is given as follows,

$$\frac{\Delta C}{C} = -\frac{0.434}{Ts^*(As^* + As')} \Delta Ts \tag{2}$$

where As' is absorbance of the solution chosen as the zero-absorbance reference, and As^* and Ts^* are As and Ts values measured against this reference solution.

The maximum precision is obtained when As^* plus As' is equal to 0.434, if As' is smaller than 0.434, and when As^* becomes zero, namely, the measured solution has the same concentration to the reference one, if As' is equal to or larger than 0.434.

Comparing Equation (2) to Equation (1), it is clear that the differential method is always more precise than the conventional method by the measurement of a given concentration, for sum of As' and As^* is the same as As and Ts^* is always larger than Ts. And moreover it is evident that the more the concentration of the reference solution approaches to that of the measured solution, the better the precision becomes.

For example, if the solution whose absorbance is 0.434, is measured by the conventional method and by the differential method used the standard solution having the same absorbance as the reference, Ts in Equation (1) is 0.368 and Ts^* in Equation (2) is unit, so the precision in the latter method is 2.7 times larger than in the former.

Although the error in Equation (1) increases rapidly——when the concentration becomes higher——, the error in Equation (2) seems to decrease if the appropriate reference solution is used. Practically, however, this is not always true. Because it is necessary to enlarge the slit width for balancing high absorbing solution, the deviation from Beer's low occurs and so Equation (2) based on the assumption of the linear relation between C and As, does not hold any more. Therefore the authors studied the precision in the determination of high concentration as follows.

If the absorbance of the solution is larger than 0.434, the maximum preci-

sion in the differential method is obtained by measuring against the reference standard solution having the same concentration to the sample as mentioned above. And in this case, the precision is calculated from the following equation that is independent to Beer's law.

$$\frac{\Delta C}{C} = \frac{(dC/dAs)_{As=As'}}{C} \Delta As \qquad (3)$$

ΔAs is the absolute error in absorbance reading at zero and is considered to be constant. So the precision is proportional to the product of the concentration by the slope of the calibration curve or of its tangent at a given concentration.

Calibration curves of phosphovanademolybdate system are shown in Fig. 1. They were obtained by the following procedures.

A proper amount of phosphoric acid solution containing from 0 to 3.5 mg of P_2O_5, were pipetted in a series of 25 ml flasks, 2 ml of 5 M perchloric acid, 2.5 ml of 0.02 M ammonium metavanadate solution and 5 ml of 0.2 M ammonium molybdate solution were added to each of flasks and diluted to to the mark. Absorbance were measured against the reagent blank at first, and then against the preceeding solution, at various given wave length.

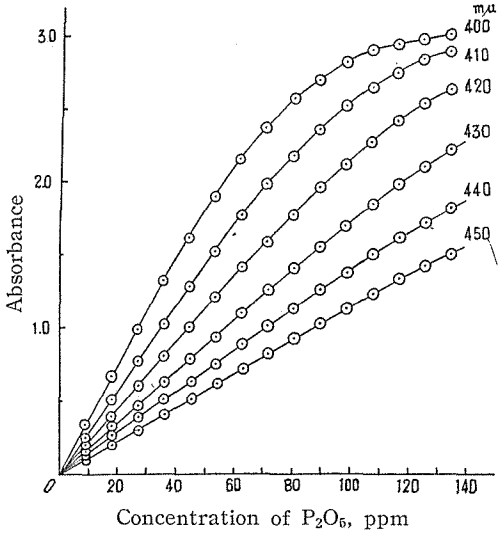


Fig. 1. Calibration curves for phosphovanadomolybdate system.

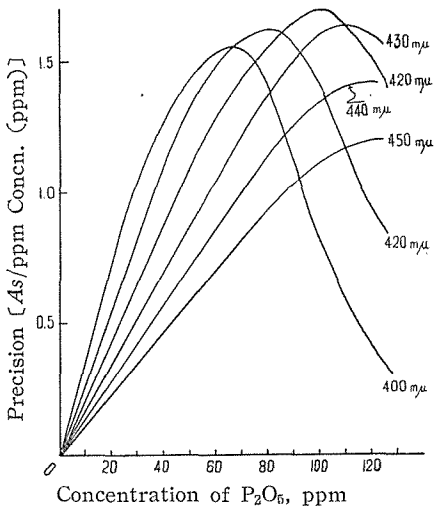


Fig. 2. Precision curves in phosphovanadomolybdate system.

From these curves, precision were calculated by Equation (3) and shown graphically in Fig. 2. As seen in Fig. 2 the maximum precision may be obtained when the solution ranging in concentration from 90 to 110 ppm of phosphorous pentaoxide is measured at 420 mμ.

As previously reported[2], phosphorous in some phosphorites could be determined spectrohotometrically with the same precision as in the gravimetric or volumetric procedures.

2. Trace Analysis Method

Trace analysis method recommended by Reilley and Crawford[3], seems to be

covenient in the determination of low concentration, but there is not any study applied to the actual analysis.

The error in trace analysis method is given as

$$\frac{\Delta C}{C} = -\frac{0.434(1-Ts'')}{Ts\,As}\Delta Ts \tag{4}$$

where Ts and As are transmittance and absorbance measured by the conventional method, and Ts'' is transmittance of the solution used as the dark—zero transmittance—reference.

The precision becomes maximum at the point of

$As=0.434$ when $Ts''\leq 36.8\%$ ($As''\geq 0.434$)

and $As=\infty$ when $Ts''\geq 36.8\%$ ($As''\leq 0.434$)

and the smaller the concentration of the reference solution, the better becomes the precision.

However, there is a limit of the concentration to be balanced, and transmittance of this least concentration is calculated from the following equation,

$$Ts''_{max.}=\left(1-\frac{1-Ts}{1-R}\right) \tag{5}$$

where Ts is transmittance of some solution and R is transmittance value of the same solution measured by setting the dark current knob to its extreme position in the clockwise direction.

As the maximum balanceable transmittance depends on electric circuit in the instrument, it may be influenced by the position of sensitivity control, at the

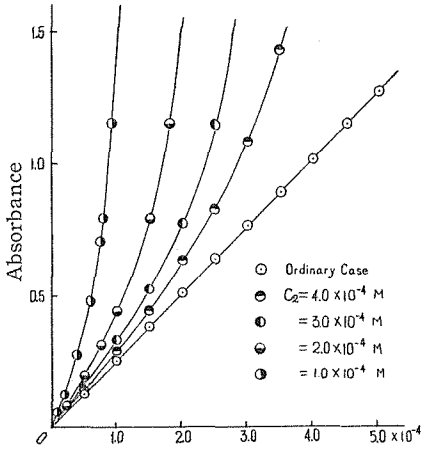
Table 1.

Wave length mμ	Concn.	As	Ts (%)	at maximum sensitivity				at minimnm Sensitivity			
				R (%)	Ts'' (%)	As''	Concn.''	R (%)	Ts'' (%)	As''	Concn.''
Phosphovanadomolybdic Acid System											
400	P_2O_5 2.0ppm	.078	83.6	46.8	69.0	.161	P_2O_5 4.1ppm	79.9	18.4	.735	P_2O_5 18.7ppm
〃	5.0	.197	63.6	<0	—	—	—	55.5	18.2	.740	18.8
〃	10.0	.387	41.0	<0	—	—	—	28.0	18.1	.742	19.1
420	2.0	.047	89.7	66.0	69.6	.157	6.5	87.3	18.9	.724	30.8
〃	5.0	.119	76.0	21.0	69.0	.161	6.7	70.0	19.3	.714	29.8
〃	10.0	.237	58.0	<0	—	—	—	48.1	19.1	.719	30.3
450	2.0	.024	94.6	82.7	68.7	.163	13.4	93.3	19.4	.712	59.4
〃	5.0	.061	86.8	57.8	68.7	.163	13.4	84.0	17.5	.757	62.0
〃	10.0	.121	75.6	21.5	69.0	.161	13.3	70.0	18.7	.728	60.2
$KMnO_4$ System											
525	$0.2\times10^{-4}M$	.051	89.0	64.7	68.8	.162	$0.63\times10^{-4}M$	87.8	18.7	.728	$2.85\times10^{-4}M$
〃	0.5	.127	74.6	17.5	69.2	.160	0.63	68.6	19.4	.719	2.82
〃	1.0	.255	55.6	<0	—	—	—	45.0	19.3	.714	2.80
〃	2.0	.510	30.9	<0	—	—	—	4.2	17.9	.747	2.93
550	0.2	.042	90.8	70.9	68.7	.163	0.64	88.7	18.6	.730	3.44
〃	0.5	.104	78.7	33.0	68.2	.166	0.65	73.8	18.7	.728	3.43
〃	1.0	.212	61.4	<0	—	—	—	52.3	19.0	.271	3.40
〃	2.0	.425	37.6	<0	—	—	—	24.3	17.6	.754	3.56

higher sensitivity position more dilute solution can be used than with lower position. On the other hand, neither wave length chosen nor the color system measured may give any effect to the limit of the transmittance.

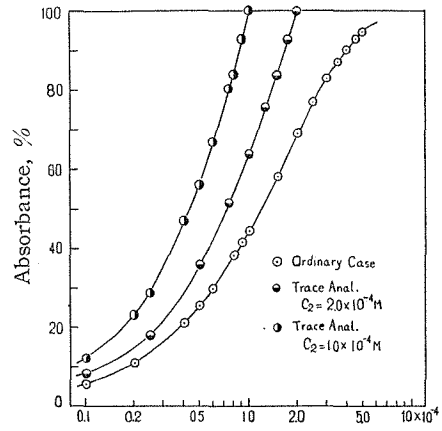
Results obtaind from phosphovanadomolybdate system and permanganate system were summarized in Table 1. The values of R were measured at the maximum and minimum sensitivity position. The results indicate that the above expectation is correct.

In order to investigate the precision of this method, calibration curves were made using permanganate system as an example. The calibration curves of the method shown in Fig. 3, have a positive deviation from the linearity. Therfore one can expect that the precision increases. Then Ringbom's calibration curves[4], some of which were illustrated in Fig. 4, were used for the quantitative consideration.



Concentration of $KMnO_4$, M

Fig. 3. Calibration curves for $KMnO_4$ system in trace analysis method.



Concentration of $KMnO_4$, M

Fig. 4. Ringbon's calibration curves of $KMnO_4$ system.

As the precision is given by

$$\frac{dTs}{dC/C}=\frac{dTs}{d\log_e C}=\frac{dTs}{2.3\log C} \tag{6}$$

without dependence to Beer's law, it is presented by the slope of the tangent on Ringbom's curves. As above mentioned, in a Beckman type spectrophotometer the sensitivity knob must be kept in the higher sensitivity range for the balancing with the dilute reference solution. Therefore the sensitivity of the null point detector is reduced. In consideration of this detectability, the slope of the curves was devided by the transmittance value resulting one unit deviation on the null point detecting scale, and the tangent was used for the comparison on precision.

In Table 2 the reproducibility of the actual measurements was shown with the value obtained by the above calculation from Ringbom's curve. Reproducibilities of the measurements in both methods are the same and have the same magnitude at least in order as that expected from the theoretical calculation of

Table 2. Reproducibility of the measurements.

I. Conventional method ($KMnO_4$ system).

Concn. of measured soln.	$4\times10^{-5}M$	$8\times10^{-5}M$	$1.5\times10^{-4}M$
As of 1st measure.	0.104	0.206	0.381
〃 2nd 〃	0.104	0.205	0.380
〃 3rd 〃	0.104	0.205	0.380
〃 4th 〃	0.104	0.205	0.381
〃 5th 〃	0.104	0.206	0.380
Average of 5 measure.	*0.104*	*0.205*	*0.380*
σ	0.00027	0.00027	0.0005
Rel. error in concn.	0.26%	0.16%	0.13%
Rel. accuracy	*1*	*1.7*	*2.0*

II. Trace analysis method ($KMnO_4$ system).

Concn. of measured soln.	$4\times10^{-5}M$	$8\times10^{-5}M$	$1.5\times10^{-4}M$
〃 reference soln.	$1\times10^{-4}M$	$1\times10^{-4}M$	$2\times10^{-4}M$
As of 1st measure.	0.276	0.795	0.792
〃 2nd 〃	0.274	0.793	0.793
〃 3rd 〃	0.275	0.789	0.790
〃 4th 〃	0.274	0.793	0.789
〃 5th 〃	0.274	0.790	0.789
Average of 5 measure.	*0.274*	*0.792*	*0.790*
σ	0.0008	0.0049	0.0018
Rel. error in concn.	0.25%	0.15%	0.11%
Rel. accuracy	*0.56*	*1.05*	*1.7*

the precision. The selection of the reference solution, with which more precise determination can be made will be discussed later in another paper.

SUMMARY

Precision of the measurements in differential and trace analysis methods was studied.

Differential method is more precise than the conventional method particularly in the determination of high concentration. On the contrary, trace analysis method seems to be useful in the determination of low concentration, but it does not mean that this method has a better precision.

In this work, errors other than that due to the transmittance reading, for instance, such as those due to the fluctuation of the light source, missetting of the reference solution, and the uncertainty in the color intensity of the colored system were not considered.

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